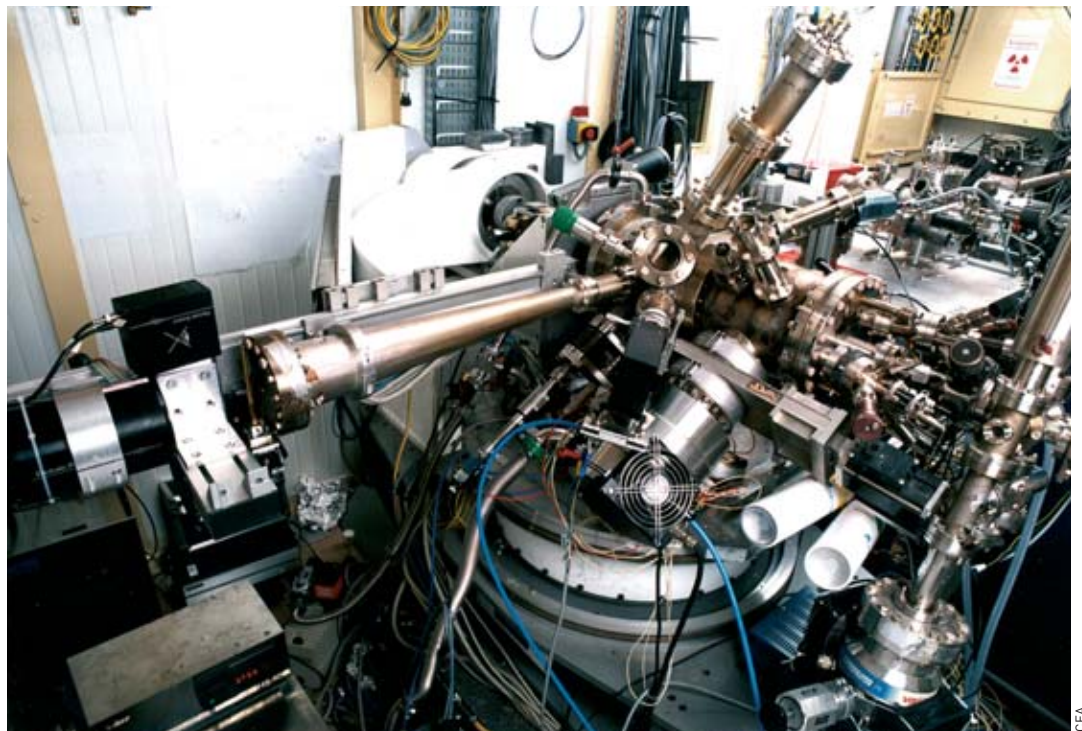


Observing the growth of nanostructures

Grazing-incidence small-angle synchrotron X-ray scattering is a tool that usefully complements microscopy measurements. It is used to monitor the evolution of the size, shape, size distribution and spatial arrangement of growing nano-objects, both on and beneath a surface. This tool can analyse, with high sensitivity, the morphology and organization of nanostructures buried under a surface and carry out measurements almost in real time in ranging environments. It opens up broad perspectives in the study of nano-objects.

Experimental setup to observe the growth of nanostructures by the GISAXS method, installed at Grenoble at the ESRF (European Synchrotron Radiation Facility).



It is well-known that a signal carrying time-dependent information can be described as a function of either time or frequency. These two descriptions are linked by a mathematical operation called a **Fourier transform**. Analogously, matter can be examined either directly, for example by electron microscopy or in a near-field imaging, or equivalently in what is called *reciprocal space*. These two representations are also linked by a Fourier transform. This operation is carried out directly when matter diffuses light. This is how **X-ray** scattering can tell us about the structure of matter at the **atomic** scale. However, it must be borne in mind that the information obtained on the structure by X-ray scattering is necessarily incomplete because only the modulus of the Fourier transform is measured, not its phase. Using an X-ray wavelength near to an **ångström**, physicists, by observing the scattering of this radiation near a direct beam (called “small-angle scattering”), can obtain information on **nanometre-**

scale structural features. If the X-ray beam is directed at grazing incidence, it will also be surface-sensitive. Accordingly, grazing-incidence small-angle X-ray scattering (GISAXS) has been developed over the last ten years as a method to characterize the shape, size and organization of **nanostructures** buried under, or deposited on, a surface.

Analysing morphology in real time

Researchers at the Materials Science Division (CEA/DSM) were the first to apply the method of grazing-incidence small-angle **synchrotron X-ray** scattering (GISAXS) *in situ*, in ultra high vacuum, during the growth of nanostructures by **molecular beam epitaxy**⁽¹⁾ (Box C, **Molecular beam epitaxy**). This method

(1) G. RENAUD, R. LAZZARI, C. REVENANT *et al.*, *Science*, 300 (5624), p. 1416, 2003.

makes it possible to analyse the morphology of these nanostructures in real time, while they are growing. This opens up the possibility of acting on the growth conditions (typically, substrate temperature and evaporation source flux) in order to optimize them. Its principle, set out in Figure 1, is very simple: a fine monochromatic parallel X-ray beam is directed at grazing incidence onto a surface, and is scattered by heterogeneities located on or under the surface. The small-angle scattering intensity is collected and measured by means of a two-dimensional detector. A beam-stop intercepts the specular beam before the detector. For objects that are far apart, the image measured is directly the average of the Fourier transform of the shape of the objects, called the *shape factor*. If the objects are close together this is multiplied by a function called an *interference function*, which takes into account their spatial arrangement.

Figure 2 shows a typical example of a GISAXS image obtained during the growth of metal nanoparticles on an oxide surface, where the objects are close together but not ordered. The dimensions in Fourier space, *i.e.*, on the image, are inversely proportional to the dimensions in real space. Thus the extension of the intensity parallel to the surface is inversely proportional to the average lateral size of the nano-objects, while the extension perpendicular to the surface is inversely proportional to their height. More precisely, oscillations in the intensity in the perpendicular direction signal the existence of two plane surfaces at the base and on the top of the objects, separated by a distance (*i.e.*, the height of the objects) that is inversely proportional to the period of the oscillations. We can also note the presence of two intensity maxima parallel to the surface on either side of the beam-stop. These maxima are due to constructive interference⁽²⁾ between the waves sent out by the neighbouring nanoparticles. They indicate that the objects are not distributed in a purely random pattern but are an average distance apart, equal to the reciprocal of the gap between the two maxima in the Fourier space. Lastly, the presence of a scattering rod 57° to the normal at the surface reveals a facet (which is perpendicular) in real space. From these observations, it is therefore possible to deduce the average shape of the objects, here a truncated pyramid, together with their dimensions and their average separation.

The reality is a little more complex: a quantitative analysis is necessary. This takes into account effects due to the *refraction* of the incident wave and its reflection off the substrate surface, and distribution over the sizes of the objects and their possible correlations. However, the shapes of fairly similar objects can be deduced by a simple qualitative analysis, which also gives their dimensions and separations to within 30% or less.

The strength of the approach developed at the CEA is that it applies this method *in situ* during growth, as

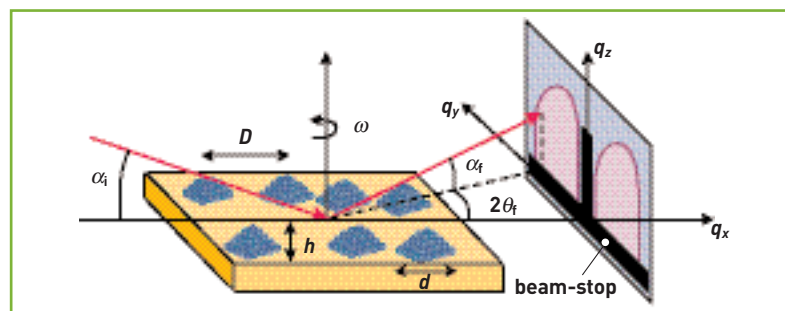


Figure 1. Schematic representation of the principle of a GISAXS measurement. The sample on which nanoscale aggregates are growing is irradiated at grazing incidence by a synchrotron X-ray beam. The scattered beam is collected in directions $2\theta_f$ in the plane and α_f out of the plane, corresponding respectively to axes q_y and q_z of the reciprocal space (*i.e.*, the image on the detector), with coordinate q_x being along the incident beam. The orientation of the incident beam parallel to the surface of the sample is defined by a rotation ω around the normal to the surface. A T-shaped beam-stop (black) stops the much more intense specular beam. The angles, of the order of a degree, are greatly exaggerated. D , h and d represent inter-island distance, aggregate height and aggregate diameter, respectively.

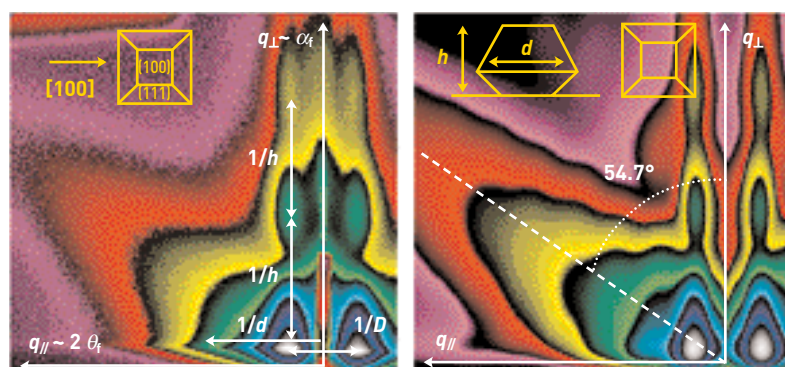


Figure 2. Left, GISAXS image obtained during the growth of palladium (Pd) aggregates on a surface of magnesium oxide MgO(100) at a temperature of 650 K. The average film thickness is 1.5 nm, which is 8 atomic monolayers. The colour scale is logarithmic and each level roughly corresponds to an order of magnitude of intensity. The noise level is about 1 cycle per second per pixel, and the useful signal is set by the limit of the detector, which is $6 \cdot 10^4$ cps/pixel. Scattering rods from {111} facets appear when the beam is directed towards the azimuth [110] of MgO. Right, simulation of scattered intensity, by modelling nanoparticles by a truncated cubo-octahedron, allowing for a size distribution. The morphological parameters are: $d = 12.6$ nm, $h = 7.9$ nm, $D = 21$ nm, half-height width of size distribution $\sigma_d = 6$ nm, $\sigma_s = 0.8$ nm.

illustrated in Figure 3. At the start of the growth of palladium on the (001)⁽³⁾ magnesium oxide surface, the scattering is widely spread, and the intensity maximum parallel to the surface (interference peak) is located far from the origin. This corresponds to the *nucleation* of small islands located close together. As the quantity deposited increases, the signal concentrates towards the origin, showing that the islands are growing. However, the interference peak does not move: this is the *growth* phase. It is followed by a continued concentration of intensity towards the origin, but this time with a concomitant shift of the interference peak in the same direction. This indicates growth and increased distance of objects, characteristic of the *coalescence* phase.

With the experimental setup developed by the CEA, counting times are short, at around a second, which makes near real time measurements feasible. In addition, the signal-to-noise ratio is very high, which allows fine quantitative analysis. It is thus possible to deduce morphological characteristics in real time during

(2) Constructive interference: there is *constructive interference* between two sine waves when they are in phase, and *destructive interference* when they are out of phase (by 180° or π).

(3) The surfaces of the monocrystals being studied are often parallel to an atomic plane in the crystal. They are then specified by the *Miller indices* (hkl) that characterize this plane in crystallography.

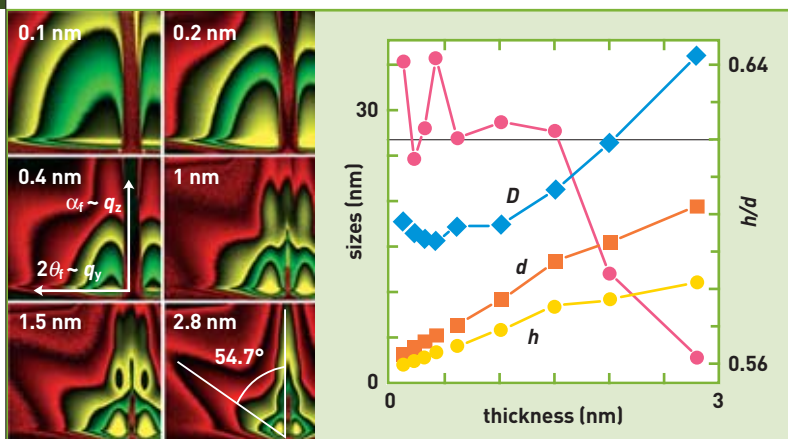
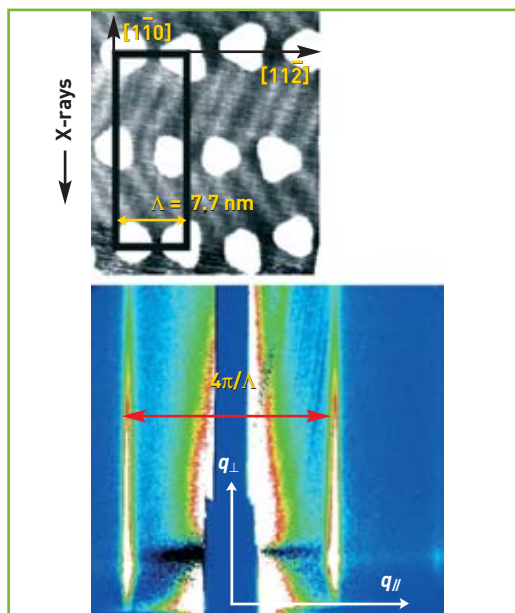


Figure 3. Left, series of GISAXS images obtained according to the thickness during the growth of palladium (Pd) aggregates on a surface of magnesium oxide MgO(001) at a temperature of 650 K. A typical effect of nucleation, growth and coalescence of aggregates is observed. Right, growth laws according to film thickness: inter-island distance D (blue), diameter d (orange), height h (yellow) and aspect ratio h/d (pink).

Figure 4. Two-dimensional array of cobalt dots on a reconstructed Au(111) surface obtained by self-organized growth. Top, a tunnelling microscope image shows that cobalt islands grow on the reconstruction nodes in a herringbone pattern on the Au(111) surface. Bottom, the rectangular super-array of dots gives rise to small angle scattering rods. Note the sensitivity of the measurement at a thickness equivalent to 0.2 Å!



growth, and so to describe growth laws, and to approach the steady-state form of **aggregates**.

Finding out the organization of nanostructures

The example presented above corresponds to the growth of objects with a broad size distribution arranged in a non-ordered pattern. However, for practical applications, it is often necessary to make nano-objects that are as similar as possible. This generally requires organized growth. GISAXS is extremely sensitive to both the size dispersal of the objects, and to their organization. This last point is illustrated on a model sys-

tem: the self-organized growth of cobalt (Co) dots on gold (Au). The (111) surface of the gold naturally possesses an ordered array of sites with locally disturbed atomic environments, which therefore form preferred sites for nucleation and subsequent growth of cobalt nanoparticles. The physicist observes, on a GISAXS image, the Fourier transform of the two-dimensional array of cobalt dots, *i.e.*, a set of rods or *Dirac comb*⁽⁴⁾, in two dimensions. Figure 4 shows an image obtained right at the start of the growth of cobalt on Au(111). It shows very fine rods parallel to the surface, showing the very high quality ordering of the dots (the Fourier transform of a **crystal** consists of very narrow peaks called *Dirac peaks*). The rods are very elongated perpendicularly, because they derive from very thin dot deposits (two atomic monolayers high).

The contribution of X-rays to the study of nano-objects

The use of a high-brilliance synchrotron X-ray source, the optimization of the experimental setup for signal-to-noise ratio and the use of a two-dimensional detector thus make it possible to study, *in situ* and in an ultra-high vacuum, the growth of nano-objects on surfaces by central scattering of X-rays. Through an accurate quantitative analysis of the signal at small angles the GISAXS method complements microscopy measurements. It provides, rapidly and in an integrated manner, the evolution of size, shape, size distribution and spatial arrangement of growing nanoparticles, in particular on insulating substrates. Growth laws can be obtained in a few hours for a broad range of parameters (flux, temperature, gaseous environment) at all growth stages from nucleation to coalescence of islands. Knowledge of these laws allows a better understanding of the physics of nanoparticle formation. Thanks in particular to its sensitivity to buried interfaces and to all degrees of lateral order, and its ability to make measurements practically in real time in various environments, the GISAXS method opens up new perspectives in crystal growth research. Possibilities include the study of growth in the presence of **surfactants**, crossing of the pressure gap in **catalytic** reactions or in vapour-phase chemical deposition, and research into self-organizing conditions. The full potential of X-rays for the study of nano-objects is obtained by combining the GISAXS method with the advantages offered by synchrotron radiation (anomalous measurement⁽⁵⁾ according to wavelength, magnetic scattering) and by wide-angle scattering⁽⁶⁾ (grazing-incidence X-ray scattering, or GIXS). This makes it possible to probe the internal atomic structure of nano-objects, in particular crystallographic orientation in relation to the substrate, how different **lattice** parameters fit into an array of **dislocations**, and the presence of structural defects.

> Gilles Renaud

Materials Science Division
CEA Grenoble Centre

(4) Dirac comb: a periodic array of infinitely fine peaks.

(5) Anomalous scattering: describes a method that consists in causing a crystal to diffract at several wavelengths near the absorption threshold of one of its elements in order to obtain information on the phase.

(6) G. RENAUD, *Surf. Sci. Rep.*, 32, Nos 1 and 2, pp. 1-90, 1998.

A From the macroscopic to the nanoworld, and vice versa...

In order to gain a better idea of the size of microscopic and nanoscopic* objects, it is useful to make comparisons, usually by aligning different scales, *i.e.* matching the natural world, from molecules to man, to engineered or fabricated objects (Figure). Hence, comparing the “artificial” with the “natural” shows that artificially-produced **nanoparticles** are in fact smaller than red blood cells.

Another advantage of juxtaposing the two is that it provides a good illustration of the two main ways of developing nanoscale systems or objects: **top-down** and **bottom-up**. In fact, there are two ways

* From the Greek *nano* meaning

“very small”, which is also used as a prefix meaning a billionth (10^{-9}) of a unit.

In fact, the **nanometre** ($1 \text{ nm} = 10^{-9}$ metres, or a billionth of a metre), is the master unit for nanosciences and nanotechnologies.

into the nanoworld: molecular manufacturing, involving the control of single **atoms** and the building from the ground up, and extreme miniaturization, generating progressively smaller systems. Top-down technology is based on the artificial, using macroscopic materials that we chip away using our hands and our tools: for decades now, electronics has been applied using **silicon** as a substrate and what are called “**wafers**” as workpieces. In fact, microelectronics is also where the “top-down” synthesis approach gets its name from. However, we have reached a stage where, over and above simply adapting the miniaturization of silicon, we also

300-mm silicon wafer produced by the Crolles2 Alliance, an illustration of current capabilities using top-down microelectronics.

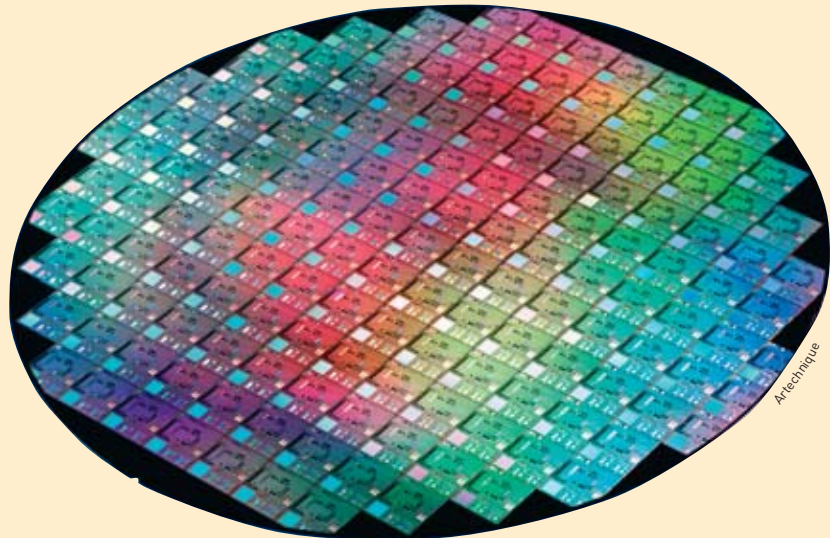
have to take on or use certain physical phenomena, particularly from **quantum** physics, that operate when working at the nanoscale.

The bottom-up approach can get around these physical limits and also cut manufacturing costs, which it does by using component **self-assembly**. This is the approach that follows nature by assembling molecules to create **proteins**, which are a series of amino acids that the super-molecules, *i.e.* **nucleic acids** (**DNA**, **RNA**), are able to produce within cells to form functional structures that can reproduce in more complex patterns. Bottom-up synthesis aims at structuring the material using

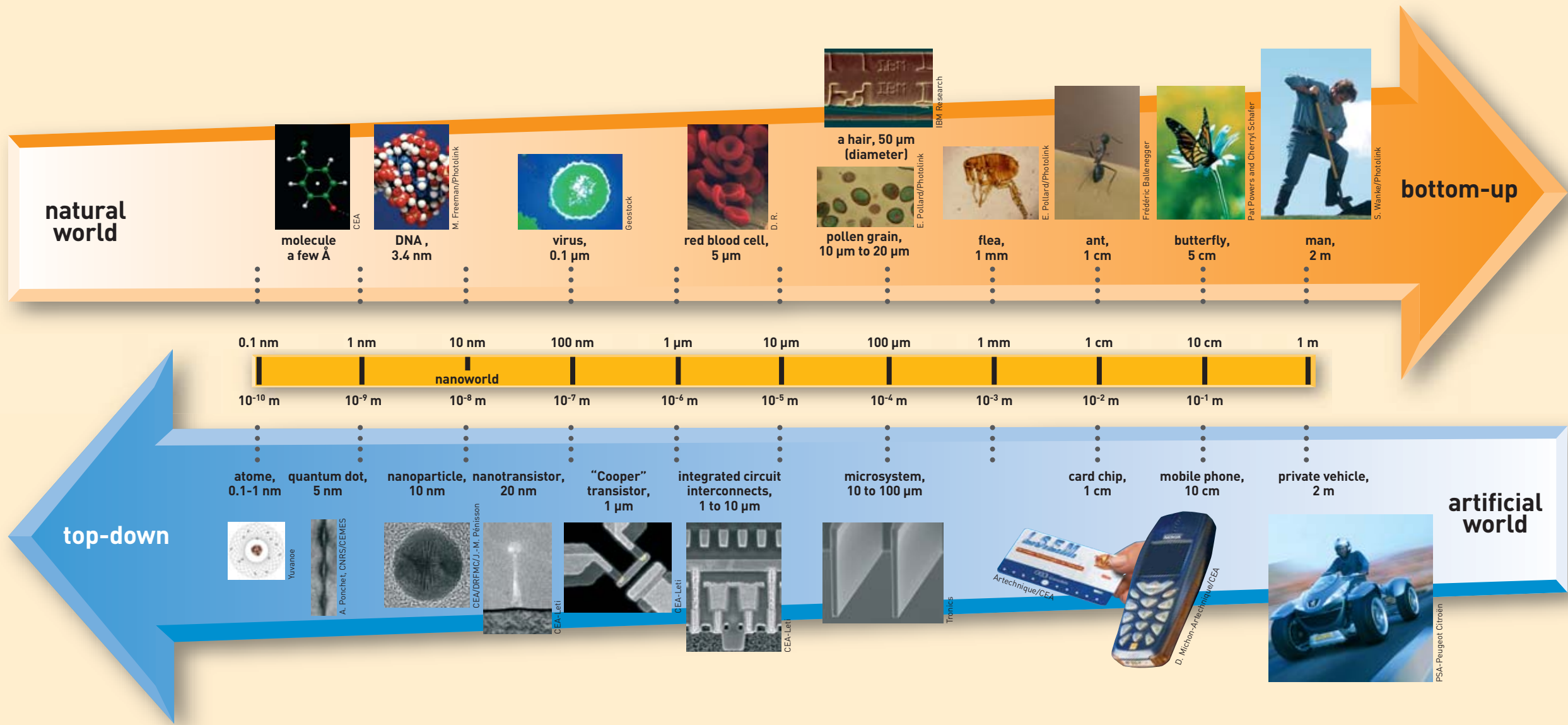
“building blocks”, including atoms themselves, as is the case with living objects in nature. Nanoelectronics seeks to follow this assembly approach to make functional structures at lower manufacturing cost.

The **nanosciences** can be defined as the body of research into the physical, chemical or biological properties of nano-objects, how to manufacture them, and how they self-assemble by auto-organization.

Nanotechnologies cover all the methods that can be used to work at molecular scale to reorganize matter into objects and materials, even progressing to the macroscopic scale.



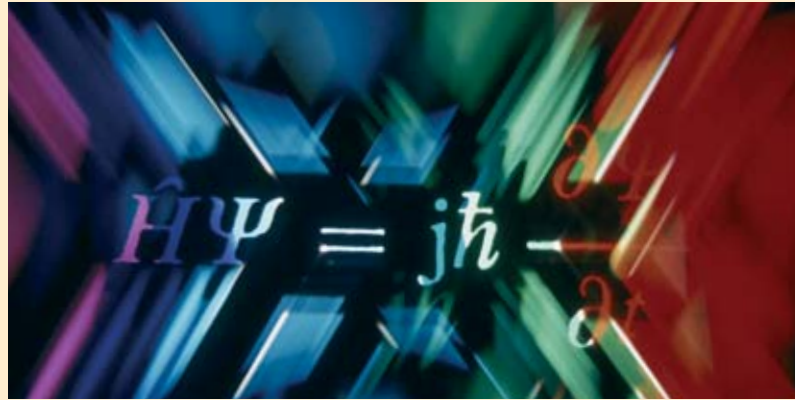
A (next)



B A guide to quantum physics

Quantum physics (historically known as quantum mechanics) covers a set of physical laws that apply at microscopic scale. While fundamentally different from the majority of laws that appear to apply at our own scale, the laws of quantum physics nevertheless underpin the general basis of physics at all scales. That said, on the macroscopic scale, quantum physics in action appears to behave particularly strangely, except for a certain number of phenomena that were already curious, such as **superconductivity** or superfluidity, which in fact can only be explained by the laws of quantum physics. Furthermore, the transition from the validating the paradoxes of quantum physics to the laws of classical physics, which we find easier to comprehend, can be explained in a very general way, as will be mentioned later.

Quantum physics gets its name from the fundamental characteristics of quantum objects: characteristics such as the angular momentum (**spin**) of **discrete** or discontinuous particles called **quanta**, which can only take values multiplied by an elementary *quantum*. There is also a **quantum of action** (product of a unit of energy multiplied by time) called **Planck's constant**



D. Sarrault/CEA

An "artist's impression" of the Schrödinger equation.

constant (symbolized as h) which has a value of 6.626×10^{-34} joule-second. While classical physics separates *waves* from *particles*, quantum physics somehow covers both these concepts in a third group, which goes beyond the simple wave-particle duality that Louis de Broglie imagined. When we attempt to comprehend it, it sometimes seems closer to waves, and sometimes to particles. A quantum object cannot be separated from how it is observed, and has no fixed attributes. This applies equally to a particle - which in no way can be likened to a tiny little bead following some kind of trajectory - of light (**photon**)

or matter (**electron, proton, neutron, atom**, etc.).

This is the underlying feature behind the **Heisenberg uncertainty principle**, which is another cornerstone of quantum physics. According to this principle (which is more *indeterminacy* than *uncertainty*), the position and the velocity of a particle cannot be measured *simultaneously* at a given point in time. Measurement remains possible, but can never be more accurate than h , Planck's constant. Given that these approximations have no intrinsically real value outside the observation process, this simultaneous determination of both position and velocity becomes simply impossible.

B (next)

At any moment in time, the quantum object presents the characteristic of *superposing* several states, in the same way that one wave can be the *sum* of several others. In quantum theory, the amplitude of a wave (like the peak, for example) is equal to a **probability amplitude** (or probability wave), a complex number-valued function associated with each of the possible states of a system thus described as quantum. Mathematically speaking, a physical state in this kind of system is represented by a **state vector**, a function that can be added to others *via* superposition. In other words, the sum of two possible state vectors of a system is *also* a possible state vector of that system. Also, the product of two vector spaces is also the sum of the vector products, which indicates **entanglement**: as a state vector is generally spread through space, the notion of local objects no longer holds true. For a pair of entangled particles, *i.e.* particles created together or having already interacted, that is, described by the *product* and not the *sum* of the two individual state vectors, the fate of each particle is linked - entangled - with the other, regardless of the distance between the two. This characteristic, also called *quantum state entan-*

glement, has staggering consequences, even before considering the potential applications, such as quantum cryptography or - why not? - teleportation. From this point on, the ability to predict the behaviour of a quantum system is reduced to probabilistic or statistical predictability. It is as if the quantum object is some kind of "juxtaposition of possibilities". Until it has been measured, the measurable size that supposedly quantifies the physical property under study is not strictly defined. Yet as soon as this measurement process is launched, it destroys the **quantum superposition** through the "collapse of the wave-packet" described by Werner Heisenberg in 1927. All the properties of a quantum system can be deduced from the equation that Erwin Schrödinger put forward the previous year. Solving the **Schrödinger equation** made it possible to determine the energy of a system as well as the **wave function**, a notion that tends to be replaced by the probability amplitude.

According to another cornerstone principle of quantum physics, the **Pauli exclusion principle**, two identical half-spin ions (**fermions**, particularly electrons) cannot simultaneously share the same position, spin and velocity (within

the limits imposed by the uncertainty principle), *i.e.* share the same *quantum state*. **Bosons** (especially photons) do not follow this principle, and can exist in the same quantum state.

The coexistence of **superposition states** is what lends **coherence** to a quantum system. This means that the theory of **quantum decoherence** is able to explain why macroscopic objects, atoms and other particles, present "classical" behaviour whereas microscopic objects show quantum behaviour. Far more influence is exerted by the "environment" (air, background radiation, etc.) than an advanced measurement device, as the environment radically removes all *superposition of states* at this scale. The larger the system considered, the more it is coupled to a large number of degrees of freedom in the environment, which means the less "chance" (to stick with a probabilistic logic) it has of maintaining any degree of quantum coherence.

TO FIND OUT MORE:

Étienne Klein, *Petit voyage dans le monde des quanta*, Champs, Flammarion, 2004.

c

Molecular beam epitaxy

Quantum wells are grown using Molecular Beam Epitaxy (from the Greek *taxi*, meaning order, and *epi*, meaning over), or MBE. The principle of this physical deposition technique, which was first developed for growing III-V **semiconductor crystals**, is based on the evaporation of ultra-pure elements of the component to be grown, in a furnace under ultra-high vacuum (where the pressure can be as low as $5 \cdot 10^{-11}$ mbar) in order to create a pure, pollution-free surface. One or more thermal beams of **atoms** or **molecules** react on the surface of a single-crystal wafer placed on a substrate kept at high temperature (several hundred °C), which serves as a lattice for the formation of a film called epitaxial film. It thus becomes possible to stack ultra-thin layers that measure a millionth of a millimetre each, *i.e.* composed of only a few atom planes.

The elements are evaporated or sublimated from an ultra-pure source placed in an **effusion cell** (or Knudsen cell; an enclosure where a molecular flux moves from a region with a given pressure to another region of lower pressure) heated by the **Joule effect**. A range of structural and analytical probes can monitor film growth *in situ* in real time, particularly using surface quality analysis and grazing angle phase transitions by LEED (*Low energy electron diffraction*) or RHEED (*Reflection high-energy electron diffraction*). Various **spectroscopic** methods are also used, including Auger **electron** spectroscopy, secondary **ion** mass spectrometry (SIMS), **X-ray** photoelectron spectrometry (XPS) or **ultraviolet** photoelectron spectrometry (UPS). As *ultra-high-vacuum* technology has progressed, molecular beam epitaxy has branched out to be applied beyond

III-V semiconductors to embrace metals and insulators. In fact, the vacuum in the growth chamber, whose design changes depending on the properties of the matter intended to be deposited, has to be better than 10^{-11} mbar in order to grow an ultra-pure film of exceptional crystal quality at relatively low substrate temperatures. This value corresponds to the vacuum quality when the growth chamber is at rest. Arsenides, for example, grow at a residual vacuum of around 10^{-9} mbar as soon as the arsenic cell has reached its set growth temperature. The pumping necessary to achieve these performance levels draws on several techniques using ion pumps, cryopumping, titanium sublimation pumping, diffusion pumps or turbo-molecular pumps. The main impurities (H_2 , H_2O , CO and CO_2) can present partial pressures of lower than 10^{-13} mbar.